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REMARKS

Entry of the foregoing, re-examination and reconsideration of the application identified in caption, as amended, pursuant to and consistent with 37 C.F.R. §1.112, and in light of the remarks which follow, are respectfully requested.

The claims have been amended at least partly in response to issues raised in the Office Action. Newly added claims 37-39 are directed to subject matter deleted from claims 1 and 2. Claims 1, 2, 4, 5, 14, 16, 29, 34 and 37-39 are currently pending in this application.

Claims 1, 2, 4, 5, 14, 16, 29 and 34 have been rejected under 35 U.S.C. §112, second paragraph, as indefinite for reasons set forth in paragraph (5) of the Office Action. Reconsideration of this rejection is requested in view of the above amendments.

The claims have been revised in response to the §112 issues raised by the Examiner. Specifically, certain optional features have been deleted from some claims and introduced as new claims. The word "characterized" has been replaced in the claims. Markush terminology has been added to claim 14. In view thereof, the §112 rejection should be withdrawn.

Claims 1, 2, 4, 5, 14, 29 and 34 have been rejected under 35 U.S.C. §102(b) as anticipated by WO 95/02314 for the reasons set forth in paragraph (7) of the Office Action. Reconsideration of this rejection is respectfully requested for the following reasons.

The presently claimed invention relates to a solid polymer electrolyte comprising a high mass or three-dimensional cross-linked methacrylonitrile homopolymer or copolymer. The solid methacrylonitrile polymer electrolytes of the invention overcome the problems

associated with the prior art use of acrylonitrile polymers as discussed on pages 2-4 of the specification. The cited WO 95/02314 publication does not disclose solid polymer electrolytes derived from methacrylonitrile.

"To anticipate a claim, a prior art reference must disclose every limitation of the claimed invention, either explicitly or inherently." In re Schreiber, 128 F.3d 1473, 1477, 44 USPQ2d 1429, 1431 (Fed. Cir. 1997); accord Glaxo Inc. v. Novopharm Ltd., 52 F.3d 1043, 1047, 34 USPQ2d 1565, 1567 (Fed. Cir. 1995). In addition, the prior art reference must disclose the limitations of the claimed invention "without any need for picking, choosing, and combining various disclosures not directly related to each other by the teachings of the cited reference." In re Arkley, 455 F.2d 586, 587, USPQ 524, 526 (CCPA 1972).

Applicants have carefully reviewed the disclosure of the '314 document and can find no mention of methacrylonitrile as a suitable monomer. It appears to be the Examiner's position that the disclosure of a derivative of acrylonitrile (page 9, line 33) would anticipate the use of methacrylonitrile. Applicants respectfully submit that this is mere conjecture and not sufficient to establish anticipation. Derivatives of acrylonitrile encompass monomeric materials such as acrylic acid and acrylamide, among others. Since there is no disclosure in the '314 document of a methacrylonitrile copolymer, the §102(b) rejection should be withdrawn.

Claim 16 stands rejected under 35 U.S.C. §103(a) as unpatentable over WO '314 in view of U.S. Patent 5,800,914 to Shiokawa et al for reasons expressed in paragraph (11) of the Office Action. Reconsideration of this rejection is requested for the following reasons.

In WO '314, the copolymer in the electrolyte is a polyacrylonitrile copolymer, i.e., it always contains acrylonitrile repeat units associated with repeat units from another monomer, for example acrylic acid, methacrylic acid or itaconic acid. In the preferred embodiment described on page 18, a polyacrylonitrile copolymer is used. No mention is made of a methacrylonitrile copolymer.

In the present invention, the polymer in the electrolyte is a methacrylonitrile homopolymer or a copolymer. As discussed on pages 2-3 of the specification, when an electrolyte containing polyacrylonitrile is used in combination with a metallic lithium electrode, "the interfacial resistance between lithium and the electrolyte steadily increases with contact time. This disadvantage is partly related to the presence, in the repeat unit, of a hydrogen carried by the tertiary carbon which is situated in the α position with respect to the nitrile group (CN). The highly electron-withdrawing effect of this nitrile group renders this hydrogen markedly more acidic. The result of this is a modification over time in the performance of the generator. The interfacial resistance gradually increases, which affects the performance of the battery, in particular the power delivered. Furthermore, thermal degradation of the PAN is reflected by the release of hydrocyanic acid (HCN), which is harmful from the viewpoint of safety of use, in particular for use by the general public. Finally, from the process viewpoint, PAN is not soluble in solvents with low boiling points. The most commonly used solvent for PAN is DMF or dimethylformamide, the boiling point of which is 152°C. Such a characteristic excludes certain processes for shaping the polymer electrolyte. This is because one of the conventional routes for the preparation of polymer electrolytes for lithium batteries consists in dissolving a polymer, a

salt and a mixture of constituent solvents of the polymer electrolyte in a common solvent, preferably with a low boiling point, and then, after having cast the mixture in the form of a film, in driving off the common solvent at atmospheric pressure or under reduced pressure without removing the constituent solvents of the plasticized polymer electrolyte. The use of a common solvent such as DMF excludes a preparation process incorporating solvents with boiling points lower than that of DMF. In other processes, the PAN + salt mixture is dissolved under warm conditions in a mixture of cyclic carbonates, before being cast in order to produce a polymer electrolyte membrane. Dissolution is carried out at an excessively high temperature which excludes, for example, the use of noncyclic carbonates." (Page 2, line 29 - page 3, line 31).

Evolution with time of interfacial resistance of PAN electrolytes in contact with a lithium electrode has been measured and the results have been published by Croce, et al., *Electrochimica Acta*, 39 (14), (1994) 2187 (copy enclosed). It appears clearly from Fig. 10 that the interfacial resistance of the lithium electrode grows over time.

Evolution with time of interfacial resistance of PMAN (polymethacrylonitrile) electrolytes in contact with a lithium electrode has been measured and compared to the results obtained and published by Croce, et al., as above mentioned. The comparison has been published in N. Chaix, F. Alloin, J-P. Bélières, J. Saunier, J-Y. Sanchez in *Electrochimica Acta*, 47 (2002), 1327-34 (copy enclosed). Fig. 2 of this document shows that upon storage of 4 days at ambient temperature, the interfacial resistance of PAN electrolyte increased by about 500%, whereas after 17 days, the interfacial resistance of PMAN electrolytes decreased by about 200%.

Since the electrochemical instability of a polymer is mainly related to the repeat unit, the behavior of isobutyronitrile (iBuCN) and pivalonitrile (tBuCN), which mime respectively the repeat unit of PAN and PMAN, was compared and the results shown in Chaix, et al. The study was performed by cyclic voltametry. When cyclic voltametry (three electrodes configuration, metallic lithium as reference electrode, platinum as working electrode) is performed at 25°C on tBuCN/LiTFSI solutions, the lithium plating/stripping efficiency remains constant and close to 50% over ten consecutive cycles. Under the same conditions, the lithium plating/stripping decreases continuously and reaches 29% at the sixth cycle. When cyclic voltametry is performed in the absence of lithium salt and lithium metal to prevent a lithium deposit which might mask other reduction reactions, i.e., using TBAP (tetrabutyl ammonium perchlorate) instead of LiTFSI, tBuCN appears markedly more stable in reduction than iBuCN.

Comparative examples were conducted by the inventors which showed that there is a substantial difference when comparing conductivity and interface resistance of a polyacrylonitrile and of a copolymer of methacrylonitrile and hydroxymethylmethacrylate (which has no acrylonitrile repeat units). The data was obtained as follows.

A polyacrylonitrile polymer (PAN) was prepared from acrylonitrile.

A methacrylonitrile copolymer (PMAN/HEMA) was prepared from methacrylonitrile and hydroxyethylmethacrylate.

Monomers were obtained from Aldrich.

Polymers were prepared in a dry box under argon by free-radical polymerization in bulk using azobisisobutyronitrile as the initiator at a temperature maintained at 80°C for 2

days. The polymer thus obtained was dissolved in dimethylketone and then precipitated in pentane under ultrasonic bath agitation. The polymer was dried for several days at 50°C in a glove box.

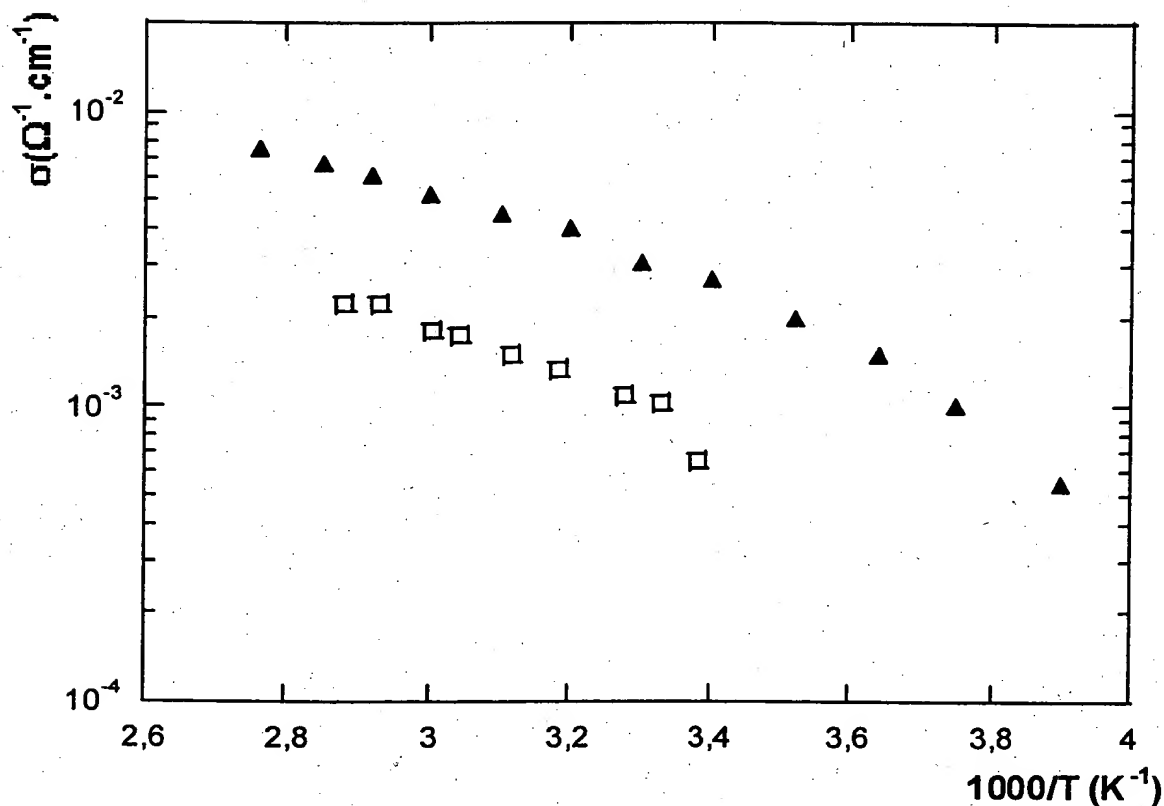
An electrolyte was prepared from PAN by dissolving PAN in anhydrous dimethyl ketone and then adding a solution of LiTFSI in a 1/1 mixture of ethylene carbonate (EC) and propylene carbonate (PC), in amounts such that PAN represents 11 % and EP/PC represents 89%, the LiTFSI concentration being 1M.

An electrolyte was prepared from PMAN/HEMA according to the following method: a solution was prepared by dissolving MAN/HEMA and hexamethylene diisocyanate (HMDI) used as a crosslinking agent, in anhydrous dimethyl ketone. HMDI is used in stoichiometric ratio with respect to the concentration of HEMA. The PMAN/HEMA ratio is 5,8/94,2 mol/mol. Then a solution of LiTFSI in a 1/1 mixture of ethylene carbonate (EC) and propylene carbonate (PC) was added, in amounts such that PMAN/HEMA represents 11 % and EP/PC represents 89%, the LiTFSI concentration being 1M.

Fig. 1 shows the conductivity σ ($\Omega^{-1}\text{cm}^{-1}$) vs the temperature $1000/T$ (K^{-1})

The conductivity measurements of the cross-linked PMAN-HEMA copolymer (black triangles) and PAN (squares), swollen with the same liquid electrolyte composition (EP/PC, 1/1, LiTFSI) and at a same ratio of liquid (89 %), shows an important gap, as PMAN-HEMA electrolyte is roughly 3 times more conductive in all the temperature ranges investigated. Thus, PMAN has more affinity than PAN for the liquid electrolyte.

Fig. 1

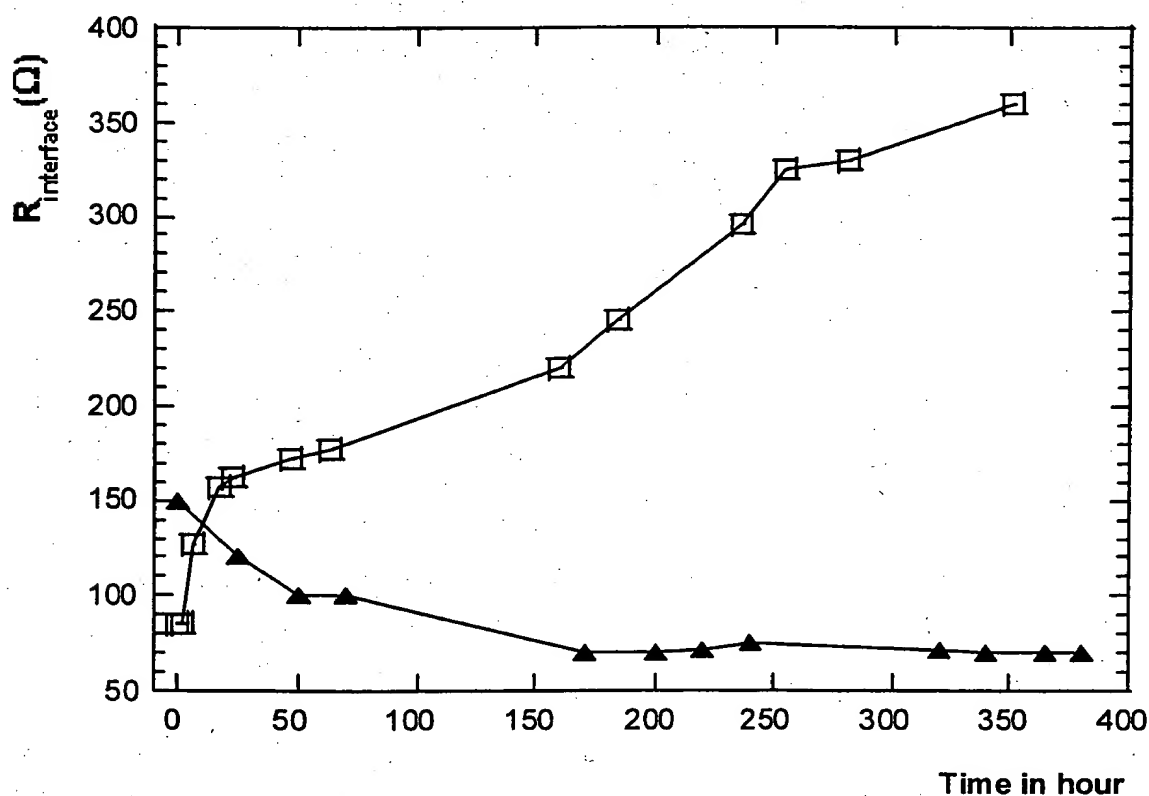


Lithium interface resistance evolution with time is a good criteria of the electrochemical stability of polymer electrolytes. The evolution with time of the interfacial resistance has been measured for the PAN electrolyte and for the PMAN/HEMA electrolyte as specified above, by impedance spectroscopy in a symmetrical cell consisting of 2 metallic lithium electrodes, in the same experimental conditions: i.e., in a glove-box under argon, at ambient temperature with the same content of the electrolyte.

Fig. 2 shows the interface resistance $R_{\text{interface}}$ (Ω) vs time, in hours.

The interface resistance increases continuously with time for PAN electrolyte (squares). This result is in agreement with Croce, et al., (Electrochimica Acta 39 (14), (1994) 2187)). On the contrary, a significant decrease with time of this interface resistance was observed for cross-linked PMAN-HEMA electrolyte (black triangles). After 350 hours, PMAN interfacial resistance is roughly 5 times lower than that measured for PAN. This clearly shows that the replacement of PAN by PMAN, greatly improves the stability in reduction. It may also be pointed out that the polymer electrolyte interface resistance is even lower than that of pure liquid electrolyte.

Fig. 2



As the above showings indicate, there is a substantial and unexpected advantage in using methacrylonitrile polymers as solid polymer electrolytes, in place of the acrylonitrile polymers of WO '314. This result could not have been predicted from the combined disclosures of WO '314 and Shiokawa '914. Accordingly, the §103(a) rejection based on these two documents should be withdrawn.

Claims 1, 2, 4, 5, 14, 29 and 34 stand rejected under 35 U.S.C. §102(b) as anticipated by or, in the alternative, under 35 U.S.C. §103(a) as obvious over U.S. Patent 5,219,679 to Abraham et al. or EP 0 798 791 for the reasons set forth in paragraph (12) of the Office Action. Reconsideration of these rejections is respectfully requested in view of the following comments.

Neither Abraham '679 nor EP '791 discloses methacrylonitrile as a suitable monomer for preparing solid polymer electrolytes. Accordingly, the §102(b) rejections based on these documents are inapplicable to the present claims, as amended, and should be withdrawn.

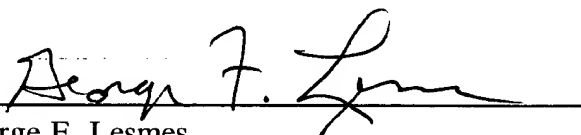
Regarding the §103(a) rejections, the use of methacrylonitrile polymers as solid polymer electrolytes provides unexpected advantages over the use of acrylonitrile polymers as fully discussed above. These unexpected advantages could not have been predicted by those of ordinary skill familiar with the disclosures of Abraham '679 or EP '791. Accordingly, the presently claimed invention is not obvious in view of the disclosures of these documents and the §103(a) rejections should be withdrawn.

In view of the above amendments and remarks, it is respectfully submitted that this application is now in condition for allowance. If there are any questions, the Examiner is invited to telephone the undersigned at (703) 838-6683 at his/her earliest convenience.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: _____


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Date: November 19, 2002

Attachment to AMENDMENT dated November 19, 2002

Marked-up Claims 1, 2, 4, 5, 14, 16, 29 and 34

Please replace claims 1, 2, 4, 5, 14, 16, 29 and 34 as follows:

1. (Amended) Solid polymer electrolyte, [characterized in that it comprises]
comprising at least one methacrylonitrile polymer chosen from:
 - linear homopolymers of high mass[, which may or may not be reinforced];
 - three-dimensional crosslinked homopolymers[, which may or may not be reinforced, rendered three dimensional by crosslinking];
 - linear methacrylonitrile copolymers of high mass; or
 - three-dimensional copolymers of methacrylonitrile and of at least one crosslinkable comonomer [which makes possible crosslinking, which copolymers are rendered three dimensional by crosslinking].

2. (Twice Amended) Solid polymer electrolyte according to Claim 1, [characterized in that] wherein the methacrylonitrile polymer is a copolymer of methacrylonitrile and of a comonomer which [makes possible the use of] is soluble in solvents with low boiling points [and/or of a comonomer which makes possible internal plasticization of the polymer by decreasing its glass transition temperature and/or of a comonomer which makes possible the introduction of a ionic functional group in order to obtain a unipolar electrolyte].

Attachment to AMENDMENT dated November 19, 2002

Marked-up Claims 1, 2, 4, 5, 14, 16, 29 and 34

4. (Twice Amended) Solid polymer electrolyte according to Claim 1, wherein [characterized in that] the methacrylonitrile polymer is a copolymer of methacrylonitrile and of at least one acrylic or methacrylic comonomer.

5. (Amended) Solid polymer electrolyte according to Claim 4, wherein [characterized in that] the methacrylonitrile polymer is a copolymer of methacrylonitrile and of at least one acrylic comonomer corresponding to the formula $\text{CHX}=\text{CZ}-\text{CO}-\text{V}-\text{Y}$, in which:

- X represents $\text{C}_n\text{H}_{2n+1}$, with $0 \leq n \leq 8$;
- Z represents $\text{C}_n\text{H}_{2n+1}$, with $0 \leq n \leq 8$, or $(\text{CH}_2)_m\text{CN}$, with $0 \leq m \leq 4$;
- V represents O, NH or NR, R represents $\text{C}_n\text{H}_{2n+1}$, with $0 \leq n \leq 8$;
- Y represents a $\text{C}_n\text{H}_{2n+1}$ radical, with $0 \leq n \leq 8$, a radical [carying] carrying an oxirane group $\text{C}_n\text{H}_{2n}-(\text{CH}-\text{CH}_2)-\text{O}$, with $1 \leq n \leq 4$, or a radical $[(\text{CH}_2)_m-\text{O}]_p\text{R}'$, in which $m = 2, 3$ or 4 , $1 \leq p \leq 50$ and R' represents $\text{C}_n\text{H}_{2n+1}$, with $0 \leq n \leq 8$.

14. (Twice Amended) Solid polymer electrolyte according to Claim 2, [characterized in that] wherein the methacrylonitrile polymer is a bipolymer of methacrylonitrile and of a monomer carrying [a] an ionic functional group selected from the group consisting of carboxylate, phosphate, phosphonate, sulfonate [or] and perfluorosulfonate [ionic functional group].

Attachment to AMENDMENT dated November 19, 2002

Marked-up Claims 1, 2, 4, 5, 14, 16, 29 and 34

16. (Amended) Solid polymer electrolyte according to Claim 4, wherein
[characterized in that] the comonomer is glycidyl acrylate or glycidyl methacrylate.

29. (Amended) Process for the bulk preparation of a methacrylonitrile polymer by
the radical route, [characterized in that it comprises] comprising the following stages:

- a thermal-decomposition free-radical initiator is dissolved in
methacrylonitrile or a mixture of methacrylonitrile with at least one comonomer,
- the mixture is degassed in order to remove the oxygen and is introduced into
a hermetically closed chamber,
- the mixture is brought to a temperature of 60 to 90°C and is maintained at
this temperature for 24 to 72 hours.

34. (Amended) Solid polymer electrolyte according to Claim 2, [characterized in
that] wherein the methacrylonitrile polymer is a copolymer of methacrylonitrile and of at
least one acrylic or methacrylic comonomer.



Pergamon

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SYNTHESIS AND CHARACTERIZATION OF HIGHLY CONDUCTING GEL ELECTROLYTES

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Abstract—The electrochemical properties of gel electrolytes formed by the immobilization in a poly(acrylonitrile) matrix of solutions of common lithium salts (eg LiClO_4 , LiAsF_6 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$) in organic solvents (eg the propylene carbonate-ethylene carbonate mixture, γ -butyrolactone or the γ -butyrolactone-ethylene carbonate mixture) have been determined. The results indicate that in accordance with previous literature data, these electrolytes have a high ionic conductivity, a wide electrochemical stability window and a high lithium transference number. However, their application in long-life, rechargeable lithium polymer batteries may be hindered by the instability of the negative electrode interface.

Key words: polymers, gel electrolytes, poly(acrylonitrile), lithium salts, ionic conduction.

INTRODUCTION

Polymers with a charge transport of the ionic type, often called "polymer electrolytes" or in a broader sense "polymer ionics", have attracted large scientific and technological interest[1]. Among the most promising, highly conducting, new generation polymer ionics are gel-type systems, as for instance those obtained by immobilizing in a poly(acrylonitrile) PAN matrix Li salt solvates in organic solvent mixtures, such as the propylene carbonate-ethylene carbonate, PC-EC mixture.

These gel electrolytes, which were originally described by Feuillade and Perche[3] and further characterized by Abraham and co-workers[1, 4, 5], are dimensionally stable and have a room temperature conductivity in the range of $10^{-3} \text{ S cm}^{-1}$. These exceptional characteristics make PAN-based gel electrolytes of immediate interest to the development of ambient temperature, advanced design, electrochemical devices.

Although gel electrolytes appear to be close to practical exploitation, their basic electrochemical properties are not yet fully understood and clarified. In an attempt to fill this gap, we have selected some representative examples of these electrolytes and investigated their behaviour in terms of bulk conductivity, electrochemical stability windows, lithium transference number and compatibility with the lithium metal electrode. The results are reported and described in this paper.

EXPERIMENTAL

Material and samples preparations

For this study we have selected six representative examples of PAN-based gel electrolytes, namely the

systems having the following molar composition:

- S-1) PAN:16/PC:23/EC:56.5/ LiClO_4 :4.5
- S-2) PAN:16/PC:23/EC:56.5/ LiAsF_6 :4.5
- S-3) PAN:16/PC:23/EC:56.5/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$:4.5
- S-4) PAN:16/BL:79.5/ LiClO_4 :4.5
- S-5) PAN:16/BL:79.5/ LiAsF_6 :4.5
- S-6) PAN:21/BL:23/EC:56.5/ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$:4.5
- S-7) PAN:21/PC:33/EC:38/ LiClO_4 :8

These compositions were determined as the most suitable for ensuring complete miscibility between the various components and thus, the full homogeneity of the final electrolytic membranes.

Lithium perchlorate LiClO_4 (Fluka, 99.5%), lithium hexafluoroarsenate LiAsF_6 and lithium perfluorosulphonimide $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (3M reagent grade), were used as received. Commercial PAN (Aldrich, reagent grade) was dried by heating it under vacuum at 80°C . Care was taken in controlling the annealing temperature in order to avoid decomposition.

Both propylene carbonate, PC and ethylene carbonate, EC (Fluka reagent grade) were purified by distillation under reduced pressure. Solid EC was mixed in the desired proportion with PC, and the resulting EC-PC liquid mixture was dried by storing it over molecular sieves. γ -Butyrolactone, BL (Fluka reagent grade) was dried by storing it over molecular sieves.

All the components, namely the selected lithium salt and PAN, were dissolved in the given organic solvent or the organic solvent mixture at temperatures ranging between 100 and 110°C . The thus obtained highly viscous solutions were cast on glass sheets to obtain the desired solid membranes, generally having a translucent, elastic appearance.

Sample characterization

The conductivity plots of the various electrolyte samples were obtained by measuring the temperature dependence of the impedance of cells formed by sandwiching the given sample between two stainless steel (SS 304) blocking electrodes. The measurements were performed using a Solartron Model 1260 Frequency Response Analyser. A thermostatic bath with 0.1°C precision was utilized to stabilize the temperature.

The cyclic voltammograms were recorded by means of a computer-controlled 273 PAR potentiostat. The electrochemical stability of the electrolytes was determined by running a sweep voltammetry on a three electrode cell where a stainless steel (SS 304) plate was the working electrode, a lithium disk was the counter electrode and a lithium strip placed between two adjacent layers of gel electrolyte, was the reference electrode.

The lithium ion transference numbers of the various selected samples were measured by utilizing both the impedance method described by Bruce and Vincent[6] and the so called "time-of-fly" method described by Watanabe *et al.*[7].

The Li/SPE (Solid Polymer Electrolyte) interfacial characteristics were obtained by monitoring the time dependence of the impedance of symmetrical Li/SPE/Li cells utilizing the same instrumentation used in the case of the conductivity measurements.

RESULTS AND DISCUSSION

1. Conductivity

Figures 1 and 2 illustrate the dependence of the conductivity of six PAN-based gel electrolytes (S-1 to S-6) samples considered in this work. The related Arrhenius plots show that the electrolytes reach conductivities of the order of $10^{-2} \text{ S cm}^{-1}$ at 60°C and that even at low temperatures (eg down to -20°C) the conductivity remains quite high (ie in the range of $10^{-4} \text{ S cm}^{-1}$).

Table 1 summarizes the room temperature conductivity of the six types of electrolytes and that of the parent liquid LiClO_4 -PC/EC solution. For allowing a direct comparison between solid and liquid electrolytes, Table 1 also reports the conductivity of a LiClO_4 -PC/EC PAN electrolyte where

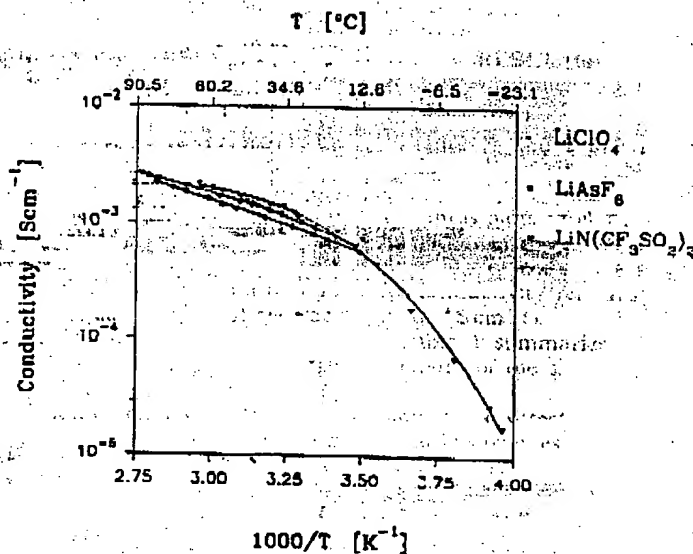


Fig. 1. Arrhenius plot of the LiX-PC/EC-PAN electrolytes $\text{LiX} = \text{LiClO}_4$ (sample S-1), LiAsF_6 (sample S-2) and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (sample S-3).

Table 1. Electrolyte conductivity at 25°C

Electrolyte	Solvent:salt ratio	Sample	Conductivity S cm^{-1}
LiClO_4 -PC/EC	8.8:1		5.2×10^{-3}
LiClO_4 -PC/EC-PAN	8.8:1	S-1	2.9×10^{-3}
LiAsF_6 -PC/EC-PAN	17.6:1	S-2	4.5×10^{-3}
LiClO_4 -PC/EC-PAN	17.6:1	S-3	4.6×10^{-3}
$\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -PC/EC-PAN	17.6:1	S-4	2.0×10^{-3}
LiClO_4 -BL-PAN	17.6:1	S-5	4.5×10^{-3}
LiAsF_6 -BL-PAN	17.6:1	S-6	6.1×10^{-3}
$\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -BL/EC-PAN	17.6:1		4.0×10^{-3}

Highly conducting gel electrolytes

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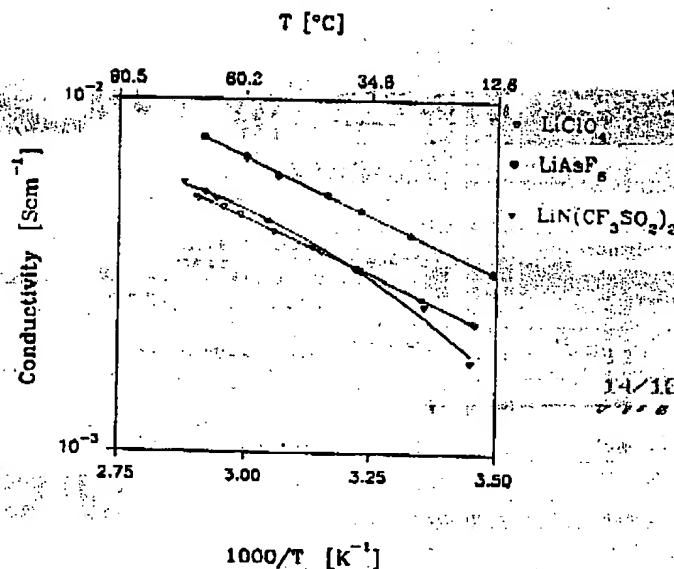


Fig. 2. Arrhenius plot of the LiClO_4 -BL-PAN (sample S-4), the LiAsF_6 -BL-PAN (sample S-5) and of the $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -BL/EC-PAN (sample S-6) electrolytes.

the solvent to salt molar ratio is 8.8:1 (sample S-7), namely equal to that of the quoted liquid LiClO_4 -PC/EC solution. The data of Table 1 clearly show that the conductivity of the gel electrolytes closely approaches that of the parent liquid organic electrolytes. This result, which confirms those already reported by other authors[4, 5], seems at a first glance to imply a close similarity between the two classes of conductors. However, as suggested by the difference in the values of the ion transference number (see the following section), the mechanism of transport is somewhat different in the two cases. A more detailed discussion on this aspect and, generally, on transport models for gel electrolytes is reported in a different paper[8]. The high conductivity is certainly one of the major features of the PAN-based ionic membranes. However, one must be aware that high conductivity is maintained, only when the electrolytes are kept in tightly closed environments. This is shown in Fig. 3, which compares the changes in resistance of

LiClO_4 -PC/EC-PAN (sample S-1) electrolyte when measured in a sealed cell and in a cell maintained open in the drybox. One can clearly see that in the former case the resistance remains practically constant for a period of 20 days while in the latter case it continuously increases. We have attributed this to a syneresis effect, namely to the fact that the gel systems are thermodynamically unstable and thus that under open-atmosphere conditions there is a progressive evaporation of excess fraction of liquid solvent. This induces a progressive increase in the viscosity of the electrolyte and thus, a decay in the ionic mobility.

2. Lithium transference number

It is today well established that the most promising positive electrodes in lithium rechargeable batteries are based on insertion compounds. Typical examples are transition metal dichalcogenides (eg TiS_2 , Nb_2S_5) and oxides (eg V_6O_{13} , LiV_3O_8). Since the electrochemical process of the electrodes consists of the intercalations and deintercalation of lithium ions throughout the host compound lattice, electrolytes with Li^+ transference number approaching unity ($t_{\text{Li}^+} \rightarrow 1$) are desirable for avoiding concentration gradient during the charge and discharge cycles. Therefore, the evaluation of this parameter is of great importance for the characterization of electrolyte materials designed for battery application.

Various methods have been proposed for the determination of t_{Li^+} in polymer electrolytes, including *dc* polarizations, *ac* impedance spectroscopy, potentiometric analysis, as well as classical Tubandt gravimetric analysis[9]. However, not all of these techniques can be correctly used since they may be affected by some operational problems which are specifically related to the nature and the characteristics of the polymeric electrolyte media, such as adhesion of the layers (which excludes Tubandt measurements) and reactivity toward the lithium

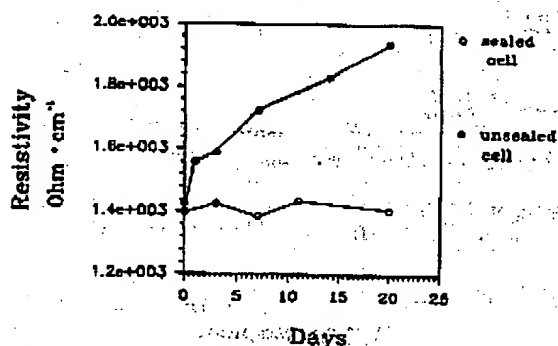


Fig. 3. Time evolution at room temperature of the resistance of a LiClO_4 -PC/EC-PAN (sample S-1) electrolyte measured in sealed and unsealed cells.

metal electrode (which affects both *dc* and *ac* analyses).

Therefore, particular attention has been devoted in the past to identify and optimize experiment techniques which would be most suitable for correct transference number measurements in polymer ionics[10]. In the specific case of poly(ethylene oxide) (PEO)-based electrolytes, Bruce and Vincent[6] have recently shown that a method based on a combination of *dc* polarization and *ac* analysis may effectively provide reproducible and reliable results. Therefore, we have considered this method also for the determination of t_{Li^+} in the PAN-based electrolytes examined in this work. Basically, the method consists of measuring by *ac* impedance and by *dc* chronoamperometry, respectively, the resistance of and the current across a symmetrical Li/electrolyte/Li cell polarized by a *dc* voltage pulse, V . The measurements are taken at the initial time of the applied *dc* voltage pulse ($t = t_0$, $R = R_0$, $I = I_0$) and under steady conditions ($t = t_s$, $R = R_s$, $I = I_s$). By using these values, the t_{Li^+} is given by the expression:

$$t_{Li^+} = \frac{I_s(V - I_0 R_0)}{I_0(V - I_s R_s)} \quad (1)$$

where V is the value of the *dc* voltage pulse applied to the cell for the chronoamperometric analysis (in the case of this work $V = 10$ mV).

Table 2 reports the values obtained for six PAN-based electrolytes and, for comparison purpose, also values of common liquid organic and PEO-based polymer electrolytes. The sequence of the values is logical since t_{Li^+} increases as the size of the anions progressively increase, namely passing from $LiClO_4$ -based, to $LiAsF_6$ -based and $LiN(CF_3SO_2)_2$ -based electrolytes. However, the values of the transference numbers of the PAN-electrolytes are much higher than those usually obtained for liquid and for PEO-based polymer electrolytes[6]. Although, this difference could possibly be related to a specific role of the polymeric matrix on the lithium ion transport mechanism[8], one has to be aware that the technique used for the t_{Li^+} determination may be associated by a certain degree of uncertainty especially in highly concentrated solutions where the extent of ion-ion and ion-solvent association is unpredictable. It may be of interest to point out that high values of t_{Li^+} have also been reported for other types of low-

viscous polymer electrolytes. For instance t_{Li^+} values of the order of 0.4–0.5 have been found by Abraham and Alamgir[12] for poly[bis-(methoxy ethoxy ethoxy) ph sphazene], MEEP-based polymer electrolytes. Furthermore, Matsuda *et al.*[13] have reported a value of $t_{Li^+} = 0.56$ for the case of a PEO-PMMA/PC- $LiClO_4$ (where PMMA = polymethylmethacrylate) system, namely of a gel electrolyte somewhat similar to those examined in this work.

We have also attempted to determine t_{Li^+} using a different technique, namely the so called "time of fly" method described by Watanabe *et al.*[7]. Basically, the method consists of polarizing a "blocking" electrode cell (eg a SS/electrolyte sample/SS (SS = stainless steel) cell) for a reasonably long time (typically 1 h) in order to promote accumulation of charge at the interface, and then following the time evolution of the current flowing through the same cell immediately after inverting the polarity of the applied voltage. The idea is to promote the separation of the ionic charge carriers during the initial long polarization period and then of monitoring the current as function of time during the reverse polarization in order to detect different peak times associated to the different mobility of the ions migrating in opposite directions.

In fact, the mobility of a given ion, μ_i can be obtained by the expression:

$$\mu_i = d^2/(V\tau_i), \quad (2)$$

where d is the sample's thickness, V is the applied voltage pulse and τ_i is the peak time. Accordingly, the lithium transference number may be evaluated by the expression:

$$t_{Li^+} = \frac{\mu^+}{\mu^+ + \mu^-} = \frac{\tau^-}{\tau^+ + \tau^-} \quad (3)$$

The t_{Li^+} values obtained with this method are generally lower than those obtained with the Bruce and Vincent's method (see Table 2). This discrepancy confirms the limitations of the experimental techniques and the qualitative character of the data of Table 2.

3. Electrochemical stability window

An important parameter for the characterization of any electrolyte, designed for battery applications is the extent of its electrochemical stability window.

Table 2. Lithium transport numbers at 25.4°C

Electrolyte	Solvent/salt ratio	Sample	$t_{Li^+}^*$	$t_{Li^+}^\dagger$
PC- $LiClO_4$	liquid		0.4*	
PEO- $LiClO_4$	polymer		0.2†	
$LiClO_4$ -PC/EC-PAN	17.6:1	S-1	0.6†	0.5§
$LiAsF_6$ -PC/EC-PAN	17.6:1	S-2	0.7†	0.6§
$LiN(CF_3SO_2)_2$ -PC/EC-PAN	17.6:1	S-3	0.8†	0.7§
$LiClO_4$ -BL-PAN	17.6:1	S-5	0.7†	0.6§
$LiN(CF_3SO_2)_2$ -BL/EC-PAN	17.6:1	S-6	0.6†	0.4§

* From reference[11].

† From reference[6].

‡ Calculated using impedance technique[6].

§ Calculated using pulse technique[7].

For instance, in the case of "conventional" rechargeable lithium batteries (ie batteries based on common intercalation cathodes, eg V_6O_{13}) the stability window of the electrolyte should be at least 4 V vs. Li. Even wider, ie exceeding 4.5 vs. Li, should be the stability window when highly oxidizing cathode materials, such as the layered $LiMO_2$ ($M = Ni, Co$) or the spinel-type $LiMn_2O_4$ compounds currently of interest for the development of high-energy lithium batteries or of high voltage lithium rocking chair batteries, are used.

For the determination of the anodic limit of the gel electrolytes we have used the generally accepted procedure, namely the determination of the current-voltage response of an "inert" test electrode (in our case, a stainless-steel (SS) electrode) in the given electrolyte. Figure 4 illustrates the current-voltage response obtained in a $LiAsF_6$ -PC/EC-PAN (sample S-2) gel electrolyte cell and, for comparison purposes, that obtained under the same sweeping conditions in a parent liquid solution. The anodic limit of the former (about 4.3 V vs. Li) is lower than that of the latter (about 5.2 V vs. Li). A similar trend has also been found for the other PAN-based gel electrolytes examined in this work (Fig. 5 and Table 3). Therefore, the addition of PAN seems to influence the oxidation kinetics. However, although narrower than that of the liquid solution, the stability window of the PAN-based gel electrolytes is still wide enough to allow safe operation with the majority of the lithium battery electrode couples.

4. Lithium plating-stripping process

The kinetics of the lithium deposition-stripping process:

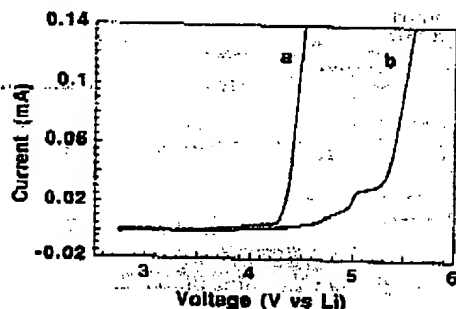
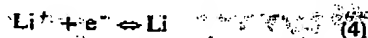


Fig. 4. Current-voltage response at 20°C of a stainless-steel electrode in a $LiAsF_6$ -PC/EC-PAN (sample S-2) electrolyte (curve a) and in a $LiAsF_6$ -PC liquid solution (curve b). Scan rate: 1 mV s^{-1} .

Table 3. Anodic decomposition voltage

Electrolyte	Sample	Decomposition voltage (volts vs. Li)
$LiClO_4$ -PC/EC-PAN	S-1	5.0
$LiAsF_6$ -PC/EC-PAN	S-2	4.3
$LiN(CF_3SO_2)_2$ -PC/EC-PAN	S-3	4.6
$LiClO_4$ -BL-PAN	S-5	4.8
$LiN(CF_3SO_2)_2$ -BL/EC-PAN	S-6	4.7

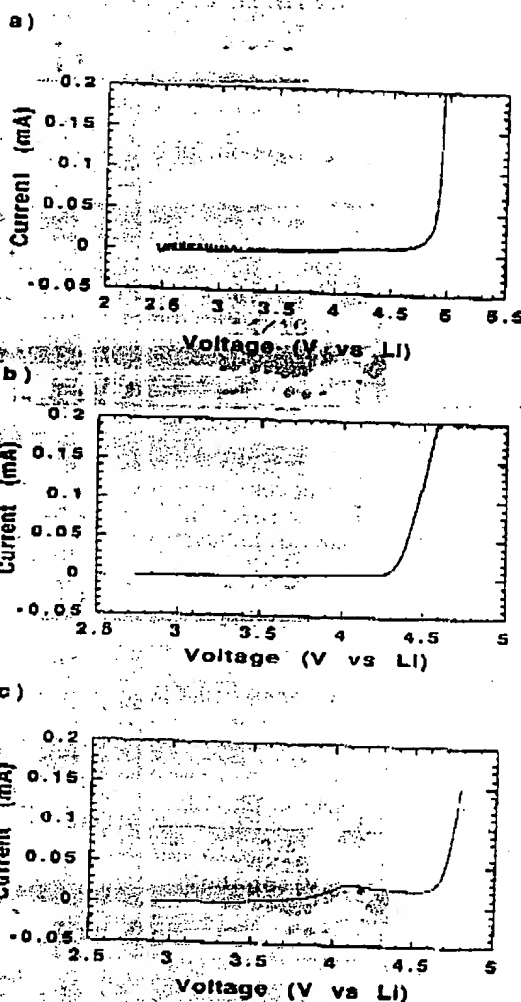


Fig. 5. Current-voltage response at 20°C of a stainless-steel electrode in PAN gel electrolytes. Scan rate: 1 mV s^{-1} . $LiClO_4$ -PC/EC-PAN (sample S-1, curve a), $LiAsF_6$ -PC/EC-PAN (sample S-2, curve b), $LiN(CF_3SO_2)_2$ -PC/EC-PAN (sample S-3, curve c).

from PAN-based gel electrolytes on metal substrates (eg stainless-steel substrates) was determined by cyclic voltammetry. Figure 6 illustrates a typical result obtained in cells using $LiAsF_6$ -PC/EC-PAN (sample S-2) electrolyte. A single cathodic deposition peak is followed by a single anodic stripping peak. The peak definition is good and the peak areas are comparable suggesting that the process is reversible, the kinetics are fast and the efficiency is high.

However, the results of Fig. 6 refer to a freshly made cell and thus, they are representative of the initial behaviour of the lithium electrode interface. To investigate the properties of this electrode on a prolonged time scale we have monitored the related voltammetry curves over a repeating number of cycles. Figure 7 shows the response of the 1st, 12th, 22nd and 62nd cycles of the Li deposition-stripping process on a SS substrate from a cell aged for one day. Some new features are evident: (i) the original single anodic stripping peak tends to split in two

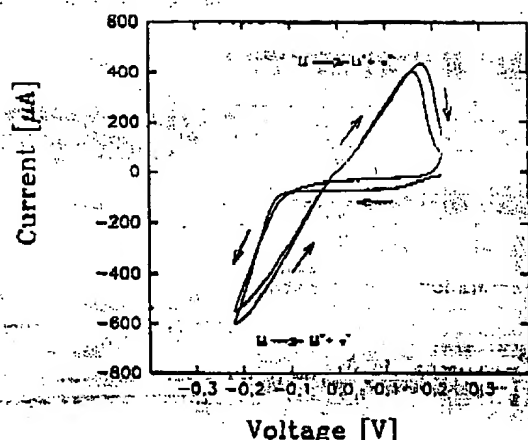


Fig. 6. Cyclic voltammetry at 20°C of a stainless-steel electrode: LiASF₆-PC/EC-PAN (sample S-2) electrolyte. Lithium reference. Scan rate: 1 mV s⁻¹.

peaks; (ii) the reversibility of the process (as expressed by the definition and the separation of the peaks) tends to decrease upon cycling. The latter effect is indicative of a progressive deterioration of the interface, possibly due to passivation phenomena (see next section). The former effect is unclear: in fact, it is difficult to explain the observed two peaks trend for the stripping process, unless assuming a formation of an intermetallic compound between the deposited lithium and the substrate.

5. Stability of the lithium electrode interface

High conductivity, high lithium transport number and wide electrochemical window, although desirable properties, are not sufficient to make an electrolyte completely useful in practical terms. The compatibility with the electrode materials is also an essential parameter to guarantee acceptable performance in electrochemical devices, *eg* batteries, especially when cyclability and reliability are considered. The trend of the cyclic voltammetry of aged cells (Fig. 7) suggests that lithium metal electrodes may undergo passivation when in contact with

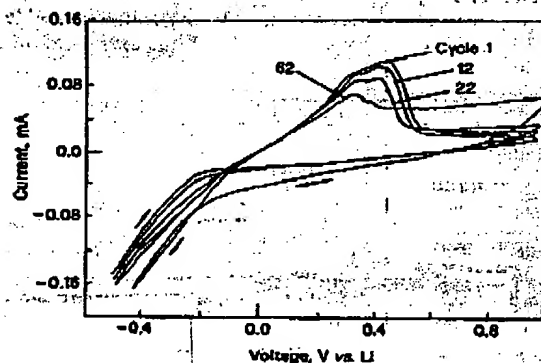


Fig. 7. Cyclic voltammetry of a stainless-steel electrode LiClO₄-PC/EC-PAN (sample S-1) electrolyte. Lithium reference electrode. Scan rate: 10 mV s⁻¹. The number of subsequent cycles is indicated in the figure.

PAN-based gel electrolytes. To further investigate this crucial aspect and in the attempt of determining the stability of the lithium interface over a prolonged time scale, we have carried out a detailed impedance analysis of symmetrical cells of the Li/electrolyte/Li type, stored and tested under different conditions.

Figure 8 illustrates the results obtained with a Li/LiClO₄-PC/EC-PAN (sample S-1)/Li cell kept continuously under open circuit conditions at room temperature. The $-jZ''-Z'$ plots reveal a progressive expansion of the middle frequency semicircle, an effect that in lithium cells may be typically related to interfacial phenomena [16, 17]. Indeed, in these cells the expansion of the semicircle may be associated with a continuous growth of a resistive layer on the lithium electrode surface. Therefore, the expansion of the impedance semicircle (Fig. 8) indicates that the lithium electrode is passivated when in contact with the PAN-based gel electrolytes. On the other hand, this behaviour, which has been also observed in other laboratories [5], is not surprising since some of the electrolyte components (*ie* EC and, particularly PC), are well known lithium corrosive agents. As previously discussed, these components diffuse from the bulk of the gel electrolyte to reach the lithium interface, thus inducing the observed passivation effects.

With the aim of further investigating these passivation phenomena and, possibly, of determining the role that also the electrolyte salts may have in its occurrence, we have followed the impedance response of Li cells using various types of PAN-based electrolytes and stored under different conditions. Figure 9 illustrates the time evolution of a Li symmetrical cell, again using the LiClO₄-PC/EC-PAN (sample S-1) electrolyte. In this case, however, the open circuit conditions have been occasionally perturbed by short potentiostatic pulses across the cell, with the intent of determining the effects of the passage of current (*eg* clearing, film disruption, and so forth) at the interface. The middle frequency semicircle again expands with a continuous trend and the short current pulses do not seem to produce any appreciable effect in controlling this tendency. This suggests that the passivation layer is quite uniform on the lithium electrode surface and

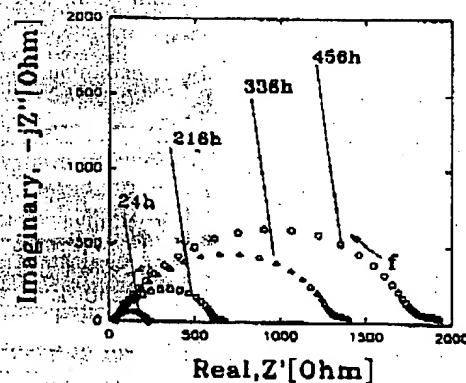


Fig. 8. Time evolution of the impedance of a Li/LiClO₄-PC/EC-PAN (sample S-1)/Li cell kept continuously under open circuit conditions at room temperature.

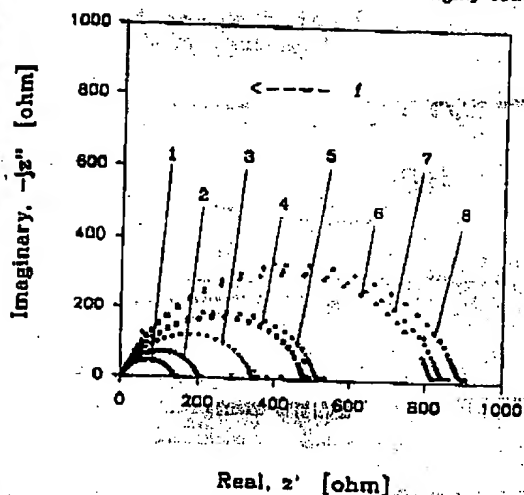


Fig. 9. Time evolution of the impedance of a symmetrical Li/LiClO_4 , PC/EC-PAN (sample S-1)/Li cell at 25°C under different conditions: (1) after assemblage; (2) after 3 h storage at OCV followed by a dc voltage (10 mV) polarization for 33 min; (3) after 21 h storage at OCV; (4) after 45 h storage at OCV; (5) after 48 h storage at OCV followed by a polarization (10 mV) for 66 min; (6) after 111 h storage in OCV; (7) after 113 h storage at OCV followed by a polarization (10 mV) for 66 min; (8) after 115 h storage at OCV.

that it cannot be easily disrupted by a modest current flow.

By using a model circuit which may be representative of the electrical equivalent of the lithium electrode interface[17], it is possible to separate the various impedance parameters which contribute to determine the evolution illustrated by Fig. 9. In this way one may obtain the time evolution of the lithium interfacial resistance as reported in Fig. 10. The trend obtained for the LiClO_4 -based electrolyte cells confirms that the passivation occurs with a continuous growth of a resistive layer at the lithium interface with a cumulative effect which appears to

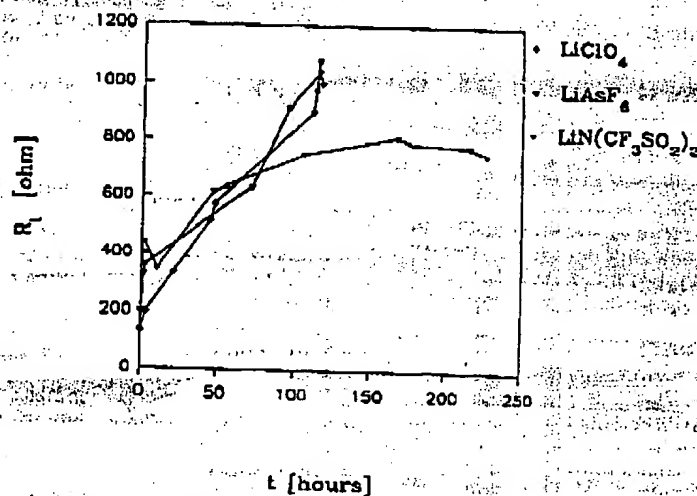


Fig. 10. Time evolution of the interfacial resistance of the lithium electrode in the LiClO_4 -EC/PC-PAN (sample S-1), LiAsF_6 -EC/PC-PAN (sample S-2) and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -EC/PC-PAN (sample S-3) gel electrolytes under the conditions described in Figs 9, 11 and 12, respectively.

become particularly dramatic as the storage time increases.

The time evolution of the impedance response of symmetrical cells of the $\text{Li/LiN}(\text{CF}_3\text{SO}_2)_2$ -PC/EC-PAN (sample S-3)/Li type is illustrated in Fig. 11. Also in this case, the middle frequency semicircle expands indicating the occurrence of lithium passivation. However, some difference both at the initial and at the final stage of the test may be noted here in respect to the previous case. Firstly, the polarization pulse is capable of reducing the expansion of the semicircle, this indicating that the growth of the

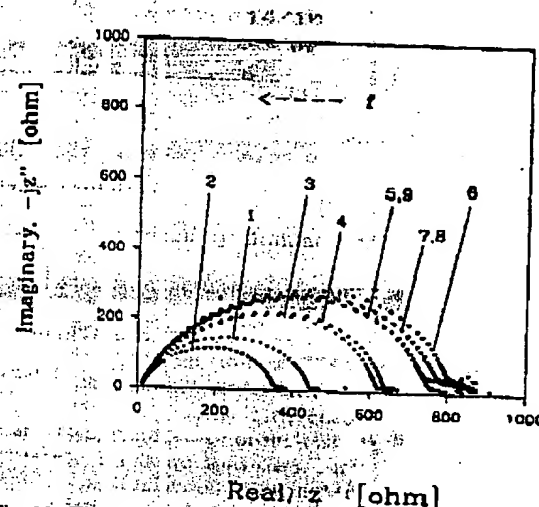


Fig. 11. Time evolution of the impedance response of a symmetrical $\text{Li/LiN}(\text{CF}_3\text{SO}_2)_2$ -EC/PC-PAN (sample S-3)/Li cell at 25°C under different conditions: (1) 1.5 h storage at OCV; (2) after 10 h storage at OCV followed by a dc voltage (10 mV) polarization for 480 min; (3) after 47 h storage at OCV; (4) after 55 h storage at OCV followed by a dc voltage (10 mV) polarization for 480 min; (5) after 105 h storage at OCV; (6) after 167 h storage at OCV; (7) 177 h storage at OCV; (8) after 215 h storage at OCV; (9) after 226 h storage at OCV.

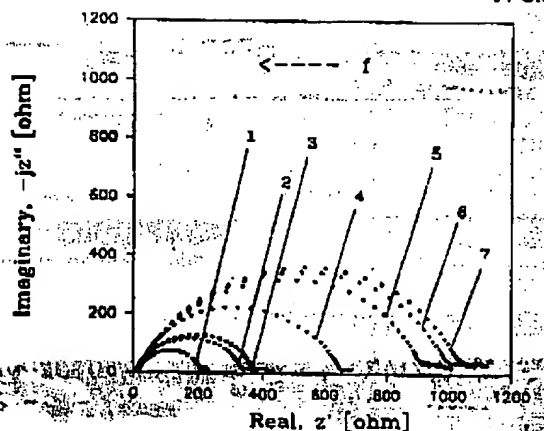


Fig. 12. Time evolution of the impedance response of a symmetrical Li/LiAsF₆-EC/PC-PAN (sample S-2)/Li cell at 25°C under different conditions: (1) after assemblage; (2) after 1 h storage at OCV followed by a dc voltage (10 mV) polarization for 0.7 min; (3) after 2 h storage at OCV; (4) after 72 h storage at OCV; (5) after 95 h storage at OCV; (6) after 115 h storage in OCV; (7) 117 h storage at OCV followed by a polarization (10 mV) for 30 min.

resistive layer can be effectively controlled by current flow through the interface. Then, we notice that the extent of the expansion progressively decreases, this suggesting that the passivation tends to reach a final level with no further progression. These aspects are confirmed by the trend of the interfacial resistance evolution reported in Fig. 10.

Finally, the time evolution of the impedance response of the third case, namely of a symmetrical Li/LiAsF₆-PC/EC-PAN (sample S-2)/Li cell is shown in Fig. 12. The response is qualitatively similar to that of the previously discussed cells. However, the comparison of the trend of the interfacial resistance (Fig. 10) reveals that the rate of passivation is different, being slow at the initial stage to then becoming progressively much faster.

In summary, the impedance analysis indicates that passivation of the lithium electrode takes place in all the PAN-based gel electrolytes here examined. On the other hand, the kinetics and the type of passivation seems to vary from one electrolyte to another, suggesting a definite role of the electrolyte salt in controlling the phenomenon. Therefore, one may hope that by the selection of a proper solvent-salt combination, the extent of the passivation may be limited to such an extent to assure acceptable stabil-

ity of the interface and thus, good lithium cyclability. It is our present aim to continue to explore this possibility with the hope of achieving a better understanding and an effective control of the passivation phenomena.

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Swollen Polymethacrylonitrile Urethane Networks for Lithium Batteries

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Copolymers of methacrylonitrile are reported. Surprisingly, their curing through urethane cross-links acts as an internal plasticization. This cross-linking prevents any dissolution or leakage, up to 90°C, when the networks are swollen by liquid organic electrolytes. These provide high conductivities, and the increase in resistivity with respect to pure liquid electrolytes remains ≤ 2 . The electrochemical investigation shows a clear improvement of stability in reduction as compared to polyacrylonitrile. The first evaluations of lithium insertion in graphite are encouraging.

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The specifications of lithium batteries intended for the electronic application imposes an operation at low temperature which can be obtained only with liquid organic electrolytes. In parallel these batteries must be able to tolerate a temperature of 80°C over a period of several days. Within the framework of cellular phone application, the tendency is to decrease volume and weight, but operational requirements, *i.e.*, accessibility of the keys, reading of the screen, make it impossible to envisage a reduction in the surface of the telephone.¹ Consequently, it is desirable to substitute prismatic batteries by flexible and thin batteries. The majority of the commercial batteries, in particular, prismatic, use a microporous polyolefin separator, which confers a particular safety, shut-down effect to the battery with respect to a great increase in temperature. However, this type of separator exhibits poor affinities for the polar organic electrolytes and makes difficult their use for the manufacture of flexible and thin batteries. An alternative to these microporous separators consists in using a polymer swollen by the liquid organic electrolytes. Thirty years ago,² these polymers swollen by the electrolyte were intended to manufacture "thin-layer" electrochemical elements. The polymers proposed were, polyacrylonitrile (PAN),^{3,4} copolymer poly(methyl methacrylate) P(AN-co-PMMA),^{5,6} polyvinyl chloride (PVC),⁷ polyacetals as polyvinylbutyral (PVB), fluoropolymers as polyvinylidene fluoride-co-polyhexafluoropropene (VDF/HFP),⁸⁻¹⁰ or PMMA copolymers.¹¹⁻¹³ The solvent retention ability of polymer gels decreases in the order of PMMA \geq PAN = poly(vinylidene difluoride) P(VdF-HFP) \geq PVdF.¹⁴ The low-affinity polymers are advantageous with respect to the mechanical strength of polymer gels but are a disadvantage with respect to ionic conductivity. It was also proposed to use poly(oxyethylene) (POE) networks.¹⁵ These adapted well to dry lithium-polymer applications but are much less interesting compared to organic solvents.

We chose to use a polynitrile because of the strong dipole moment of the nitrile group and the affinity of PAN for the usual lithium salts and the polar solvents which constitute the liquid electrolyte. However, the electrochemical instability of PAN with a lithium negative electrode has been known for a long time and has been highlighted from measurements of PAN electrolyte/lithium interface resistances and their evolution with time.¹⁶ We attributed much of the PAN instability to the existence of the rather "acidic" hydrogen in the alpha position of the nitrile group. To solve this we chose polymethacrylonitrile (PMAN) in which a methyl group replaces this hydrogen. PMAN's ability to complex the lithium cation^{17,18} was recently studied by IR spectroscopy and differential scanning calorimetry (DSC). In fact, PMAN allows one to dissolve varied lithium salts up to very high concentrations.

A comparative study of the electrochemical stability of polynitriles was recently carried out through model molecules,¹⁹ isobuty-

ronitrile (iBuCN) and tertibutyl nitrile (tBuCN) which reproduce the polymer repeat units of PAN and PMAN, respectively. This study showed without ambiguity that iBuCN is definitely less stable in reduction than tBuCN, even in the absence of lithium, while iBuCN is slightly more stable in oxidation than tBuCN.

PMAN has many advantages with respect to PAN: (i) a good solubility in various solvents, making easier the films casting method, and (ii) a much weaker release of cyanhydric acid during a thermal degradation,²⁰ which leads mainly to the PMAN depolymerization. But contrary to PAN, whatever its molecular weight, it does not lead to physical gels with the usual organic electrolytes. As a consequence, the swelling of unidimensional PMAN homopolymers by liquid organic electrolytes results in very poor mechanical properties. In order to overcome this drawback we partially cross-linked a PMAN homopolymer by UV insolation in the presence of monomers with a functionality equal to four.¹⁸

Despite its convenience, this method does not allow a control of the cross-links distribution and is not adapted to all kinds of processes as it imposes a UV exposure of the polymer electrolyte. An alternative consists in preparing unidimensional prepolymers with a function allowing their further cross-linking. The syntheses of prepolymers, carried out by free-radical polymerization, gives access to a broad variety of copolymers. We present the networks formed by polyaddition between copolymers of methacrylonitrile/hydroxyethyl methacrylate and diisocyanates.

Experimental

Methacrylonitrile obtained from Aldrich was distilled before use and maintained at near 0°C. Hydroxyethylmethacrylate, butylmethacrylate, and poly(ethylene glycol)ethyl ether methacrylate Mn = 246 g/mol were used as received. The lithium salt LiTFSI, obtained from Fluka, was dried at 100°C under vacuum for 48 h and then stored in a glove box. LiPF₆ obtained from Merck was stored as received in a glove box. The graphite electrode was prepared with 74.9% of superior graphite (LBG50, 3-24-1) mixed in dibutyl phthalate DBP, with 15% PVdF-HFP copolymer and 10% acetylene black. The electrode washed with methanol (to remove DBP), dried 24 h at 60°C in vacuum, and was then stored in glove box under argon.

The different copolymers were obtained by free-radical polymerization in bulk using azobisisobutyronitrile as the initiator. The temperature was maintained at 80°C for 2 days. The polymer thus obtained was dissolved in dimethyl ketone and then precipitated in pentane agitated by an ultrasonic bath. The method of ultrasonic stirring yields better polymer dispersion, and so higher polymer purity was obtained. The material was dried for several days at 50°C under vacuum.

All sample preparations were carried out in an argon dry box. The swollen network electrolytes were prepared according to the following process: Solutions were prepared by dissolving the copolymer and a diisocyanate, used as a cross-linking agent in anhy-

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Table I. Determination of the composition of copolymers by ^1H NMR, MWD of terpolymers.*

	HEMA (mol%) In the initial monomer mixture	HEMA (mol%) Incorporated in the copolymer	BUMA (mol%) In the initial monomer mixture	BUMA (mol%) Incorporated in the copolymer	PEGEEM (mol%) In the initial monomer mixture	PEGEEM (mol%) Incorporated in the copolymer	Mw(g/mol)	$I = \text{Mw/Mn}$
B1	3	5.8		
B2	5	7		
B3	10	17.4		
T1	3	5.5	5	7.3	89,000	1.2
T2	3	7.9	10	13.2	189,000	1.4
T3	3	6.5	20	21.7	600,000	1.9
T4	10	14.7	5	5.4	36,900	1.5
T5	10	15.3	10	11.9	116,800	1.3
T6	10	11.1	20	19.4	305,400	1.6
T7	2.8	5.1	3.7	4.7	184,000	4.1
T8	2.8	9.4	5.6	5		
T9	2.8	9.8	7.2	11		

* Mw expressed in polystyrene equivalents.

drous dimethyl ketone. Sometimes the liquid electrolyte was added to the previous solution. According to the typical casting procedure, the dimethyl ketone solution was cast in a glass ring on a poly(tetrafluoroethylene) (PTFE) plate. The dimethyl ketone was then evaporated and the resulting film cross-linked at room temperature in a glove box via the formation of urethane bonds. According to the diisocyanate used, the cross-linking was performed for 1 day with tolylene-2,4-diisocyanate (TDI) and 2 days with hexamethylene diisocyanate (HMDI).

To calculate the percentage of insoluble material, the films were swollen and washed several times in dimethyl ketone. Afterward they were dried at 50°C under vacuum for 24 h. The weight difference between the latters and the initial films, i.e., before swelling, allows the insoluble rate to be determined.

Glass transition temperatures, T_g , were measured under helium or argon flow on a Netzsch STA409 Thermal Analyzer. Using a typical procedure, samples were cooled rapidly from room temperature to -100°C . Then the samples were heated to 100°C at $10^\circ\text{C}/\text{min}$ increments. The first scan was stopped at 100°C to prevent potential PMAN cyclization. During the second scan the samples were heated to 150°C . T_g values were determined from the second scan. Swollen network electrolytes were analyzed at lower scan speed, i.e., $5^\circ\text{C}/\text{min}$, to get a good stabilization of heat flow in the low-temperature domain.

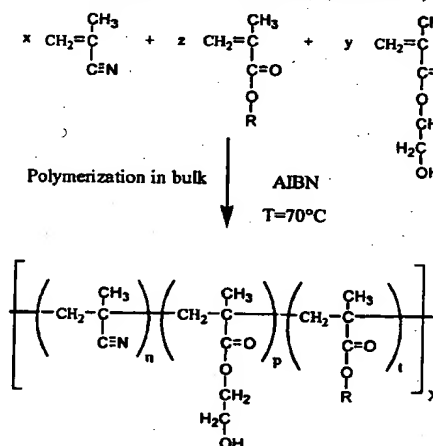
Gel permeation chromatography (GPC) analyses were performed in tetrahydrofuran (THF), filtered ($0.4\ \mu\text{m}$) and degassed beforehand, on a Waters 590 GPC instrument equipped with a differential refractometer Waters 410 and a Waters 745B "data module". Samples were analyzed, through three ultrastaygel columns of 500, 10^3 , and $10^4\ \text{\AA}$, at a solvent flow rate of $1.2\ \text{mL}/\text{min}$. Average molecular weights were calculated in equivalent polystyrene, using the calibration curve established from polystyrene standard samples.

Ionic conductivities of the lithium salt/polymer complexes were determined, under argon, by impedance spectroscopy over the frequency range 5 Hz to 13 MHz, using stainless steel blocking electrodes and an HP 4192A analyzer.

Voltamperometry was performed using a three-electrode configuration cell. Stainless steel was used as the working electrode while two lithium metallic foils were used as the reference and auxiliary electrodes. Experiments were carried out under argon with a scanning rate of $7.5\ \text{mV}/\text{min}$ using a MacPile computer. The same three-electrode configuration was used for the characterization of the composite electrodes.

Results and Discussion

Synthesis and characterization of the copolymers.—Free-radical polymerization of methacrylonitrile (MAN) lead to fully amorphous polymers. The same goes for alkylmethacrylate and oligo(oxyethylene) methacrylate, providing that the alkyl and oligo(oxyethylene) dangling substituents are short enough to avoid side-chain crystallization. Copolymers consisting of these monomers are therefore amorphous. The reactivity ratios of MAN and methacrylate are close enough to expect the monomer repeat units to be randomly distributed in the copolymer chains.^{21,22} In MAN copolymers hydroxyethylmethacrylate (HEMA) is intended to provide a network through the reaction of its primary alcohol function with a diisocyanate. A third methacrylate monomer may be used in order to induce an internal plasticization of the copolymer. For this purpose we selected either an apolar dangling substituent, butyl, with butylmethacrylate (BUMA), or a polar one oligo(oxyethylene) with poly(ethylene glycol) ethyl ether methacrylate (PEGEEM) (Scheme 1). Compositions



$\text{R} = -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$

Butyl methacrylate BUMA

$\text{R} = -(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_2-\text{CH}_3$

Poly(ethylene glycol) ethyl ether methacrylate

of copolymers MAN/HEMA and terpolymers MAN/HEMA/BUMA or MAN/HEMA/PEGEEM were determined by ^1H NMR (Table I).

Table II. Comparison of T_g between prepolymers and related networks.

Copolymer	Calculated T_g of prepolymers (°C)	T_g of Prepolymers (°C)	T_g of urethane (TDI) networks (°C)	T_g of urethane (HMDI) networks (°C)
B1	115	92.8	74.1	49.2
B2	113	78.8	55.2	45.7
B3	106.3	95.8	63.5	41.1
T1	91	98.4	...	57.7
T2	84	90.8	64.6	63.5
T3	73	80.4	66.5	66.6
T7	60	77.8	51.9	56.5
T8	57	67.7	56.3	49.5
T9	20	66.5	55.2	53.3

MAN/HEMA copolymers with different MAN/HEMA ratios were obtained. To the best of our knowledge, MAN/HEMA reactivity ratios have not been reported. From the nuclear magnetic resonance (NMR) data, HEMA seems to be more reactive than MAN (Table I). In terpolymers (Table I) HEMA appears still more reactive than MAN, but its proportion depends on the third comonomer ratio. The NMR data show that PEGEEM and BUMA are also more reactive than MAN. In the case of MAN and BUMA, the reactivity ratios ($r_1 = 0.56$ and $r_2 = 0.75$)²² calculated for a MAN/BUMA copolymerization are in agreement with our results.

Molecular weight.—The molecular weight distribution (MWD) was characterized by GPC in THF, and the average molecular weights (M_w), M_n , and the polydispersity index (I) were calculated from a calibration curve in polystyrene (Table I). MAN/HEMA copolymers prepared in bulk probably have molecular weights which are too high to prevent their dissolution in THF. On the other hand, the dissolution and analysis by GPC of dipolymers prepared in solution was successful and provided for this sample: $M_w = 70,000$ g/mol, $M_n = 40,000$ g/mol, and $I = 1.75$.

Due to the presence of the third monomer unit, most of the terpolymers prepared in bulk, even of high molecular weight, are soluble in THF. Medium to fairly high molecular weights were obtained for the terpolymers BUMA/HEMA/MAN; however, these values were not obtained from light scattering or membrane osmometry. We are confident with the molecular weight distributions and the relatively low polydispersity index, around 1.5, must be emphasized.

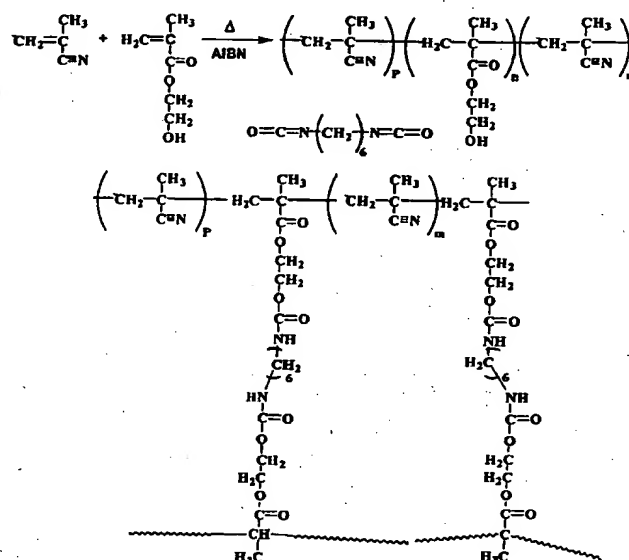
According to the content in PEGEEM, terpolymers are soluble or insoluble in THF. Even the insoluble terpolymers are not cross-linked as they are soluble in dimethyl ketone. Contrary to the previous BUMA/HEMA/MAN terpolymers, PEGEEM/HEMA/MAN samples soluble in THF exhibit a wide molecular weight distribution with a polydispersity index ≥ 4 . This discrepancy with the values obtained for BUMA/HEMA/MAN terpolymers might be attributed to transfer reaction, and probably branchings, involving the oligo(oxyethylene) side chain of PEGEEM.

Thermal properties.—DSC analyses performed on all these samples confirm their amorphous character. The empirical relation $1/T_g = W_A/T_{gA} + W_B/T_{gB}$ allows the T_g of a statistical copolymer polyA-co-polyB to be predicted roughly. W_A and W_B are the mass fractions of polyA and polyB in the copolymer, respectively, while T_{gA} and T_{gB} are the glass transition temperatures of the homopolymers polyA and polyB. The Polymer Handbook²³ provides conflicting data on T_g of polyHEMA, with values ranging between 328 and 359 K. PolyBUMA has a T_g close to 293 K and PEGEEM has a T_g close to 175 K. As the T_g of PMAN is around 393 K, one may expect that MAN copolymerization with these monomers more or less induces an internal plasticization. Table II, which lists T_g values

of these copolymers, is in agreement with this internal plasticization assumption. All these samples exhibit lower T_g than PMAN homopolymer ($T_g = 120^\circ\text{C}$), but if T_g values of MAN-HEMA copolymers are always lower than those predicted by the Fox equation, T_g measured for terpolymers is higher than predicted.

In the MAN/HEMA copolymers, the incorporation of the HEMA unit results in a slight but continuous decrease in the T_g values up to 7 mol%. Thereafter a higher T_g , but still lower than that of PMAN, is obtained for a HEMA molar composition of 17.4%. It might be assumed that at high HEMA content, interchain hydrogen bonds between two hydroxy groups behave as physical cross-links, decreasing the chain mobilities and thus increasing T_g . For both kinds of terpolymers, T_g decreases markedly when the concentration of the third comonomer increases. In agreement with the T_g of polyBUMA and polyPEGEEM homopolymers, T_g decreases more for PEGEEM/HEMA/MAN terpolymer.

Synthesis and characterization of the networks.—TDI and HMDI were used to cross-link, in bulk, the copolymers through the formation of urethane bonds (Scheme 2). The content of insoluble poly-



mer depends on the cross-linking process. Indeed, the cross-linking may be performed either on a dry copolymer, e.g., free of any solvent and salt, or on a copolymer swollen by the liquid electrolyte. The percentage of insoluble polymer was determined on cross-linked polymer membranes in two ways, first without solvent and salt and after with the liquid electrolyte. Without solvent our membranes presented a very high insoluble rate, nearly 90%. In the presence of electrolyte the cross-linking reaction is also efficient, as an insoluble rate near 80% was obtained.

Surprisingly, we noticed a spectacular decrease in T_g value for all our membranes whatever curing agent, HMDI or TDI, was used (Table II). This effect is more noticeable, however, when HMDI is used as curing agent. An increase in cross-link density is associated to a decrease in available free-volume, and T_g value is expected to increase. Such behavior was reported by Carvalho *et al.*²⁴ with polyether-urethane networks. As the decrease in T_g is observed both with a flexible diisocyanate, HMDI, and with a rigid one, TDI, the internal plasticization induced by the curing agent is not the sole factor. It may be assumed that cross-linking spreads the polynitrile chains, therefore minimizing the nitrile/nitrile Van der Waals interactions, which is great in the case of polar groups. Such T_g decrease

Table III. Conductivity values of swollen electrolyte networks at different temperatures based on cross-linked copolymers.

	Temperature				
	-20°C	20°C	60°C	90°C	
EC/PC (1/1)	1.64	5.59	11.3		
LiTFSI 1 M					
B1	0.56	2.69	5.55	7.7	σ (mS cm ⁻¹)
B2	0.78	3.25	6.51	8.7	
B3	0.8	2.99	5.82	7.5	
T1	0.61	2.3	4.53		
T3	0.63	2.14	4.1		
T4	0.46	1.75	3.54		
T5	0.53	1.7	...		
T6	0.41	1.56	3.02		
T7	0.84	2.99	...		
T8	0.81	2.73	4.13		
T9	0.72	2.26	4.62		

was already reported for complexes of lithium salt and PMAN¹⁹ and explained by a preferential interaction between CN and lithium cation.

T_g values near 40°C could be obtained, 80°C lower than that of PMAN. Surprisingly, the membranes obtained using bipolymers presented the lowest T_g values. As the decrease in T_g might be related to unreacted diisocyanate acting as an external plasticizer rather than to cross-linking, we performed comparative DSC analysis between unwashed and washed membranes. We found that not only does the washing not result in a T_g increase but the washed membrane exhibited T_g lower, 49°C, than that obtained with the unwashed one, 60°C.

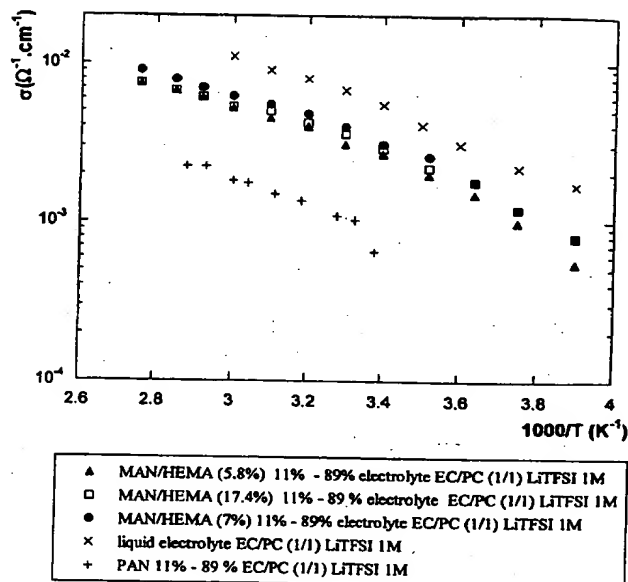
In our study the cross-linking is therefore the best internal plasticization. As we obtained lower T_g values with HMDI, we used these compounds for the electrochemical investigation in the following studies.

Ionic conductivities.—Due to the solubility of the linear copolymers in liquid electrolytes, ionic conductivity measurements were restricted to the networks. They were performed on networks swollen by two kinds of liquid electrolytes. The first one, consisting of a LiTFSI 1 M solution in an EC/PC mixture (1/1 in volume), might be used in nonrechargeable lithium batteries, as LiTFSI has a good stability with metallic lithium.²⁵ To some extent it might also be used in lithium rechargeable batteries, whose lifespan is limited. However, LiTFSI induces a corrosion of aluminum current collectors,^{26,27} and this liquid electrolyte is thus not suitable for lithium-ion batteries, despite its high viscosity. The second kind of liquid electrolyte thus consists of LiPF₆ 1 M in solution in a ternary mixture ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 2/2/1 in volume).

Ionic conductivity of networks swollen by LiTFSI electrolyte.—The conductivity measurements were performed on swollen network electrolytes with the following composition in weight

Copolymer 11%, 89% EC/PC (1/1 in volume) 1 M LiTFSI and obtained by swelling the network with a 1 mol L⁻¹ solution of LiTFSI in a 1/1 mixture (in volume) of EC and PC.

Table III lists the conductivities at different temperatures, namely, -20°C, 20°C, 60°C and, in the case of the more conductive electrolytes, up to 90°C. All the membranes exhibit high conductivities. The less conductive ones are based on MAN/BUMA/HEMA networks but nevertheless reach 2 mS/cm at 20°C. At -20°C MAN/HEMA/PEGEEM networks are only slightly more conductive. Therefore, due partly to the internal plasticization provided by HMDI curing agent, the best networks are also the simplest ones, i.e., MAN/HEMA networks. The measurements carried out on various membranes show good reproducibility. The conductivity measurement accuracy is evaluated at $\pm 3 \times 10^{-4}$ S/cm. The ability of MAN/HEMA network electrolytes to endure a temperature of 90°C

Figure 1. Conductivity plots vs. T^{-1} : comparison between liquid electrolyte, swollen MAN/HEMA networks, and gelled PAN.

without damage must be emphasized. Indeed, not only no mechanical damage is observed as a result of this heating but the ionic behavior is retained, as the conductivity curves obtained by cooling from 90 to -20°C are perfectly superimposed on that obtained by heating from -20 to 90°C.

Arrhenius plots of MAN/HEMA network electrolytes, in the whole temperature range Fig. 1, are compared with the conductivity of pure liquid electrolyte and the conductivity for PAN swollen by a similar electrolyte. The figure illustrates the temperature dependence of conductivity with HEMA composition. Conductivities near 3×10^{-3} S/cm at 20°C were obtained with all the samples. The mem-

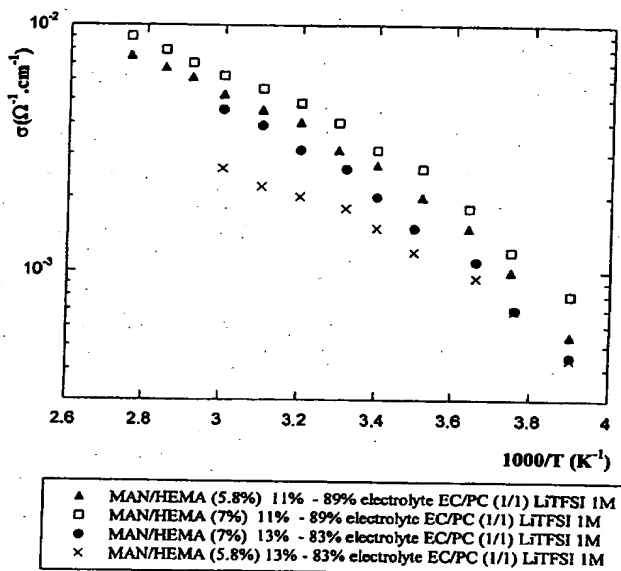


Figure 2. Conductivity comparison between B1 and B2 networks, swollen, at 83 and 89%, by a molar solution of LiTFSI in EC/PC (1/1 in volume).

Table IV. Comparison of the VTF parameters of liquid electrolyte and those of swollen electrolyte networks based on cross-linked MAN/HEMA dipolymers.

Electrolyte	T_0 (°C)	E_a (eV)
EC/PC (1/1) + LiTFSI 1 M	-136	0.058
B1 + 89% liquid electrolyte	-86	0.03
B2 + 89% liquid electrolyte	-90	0.03
B3 + 89% liquid electrolyte	-90	0.029

brane B2 consisting of 7% HEMA is slightly more conductive. Except at the lowest temperature, *i.e.*, -20°C, where the conductivity gap between our networks is 40%, this gap remains around 20%. This might be explained by two opposing effects. Indeed, the increase in cross-link density should decrease the conductivity, while the internal plasticization, induced by HMDI curing agent, should increase it.

The gap between the previous network electrolytes and that based on swollen linear PAN is far greater and ranges between 380 and 480% according to HEMA composition. The nature of the swollen polymer PMAN or PAN therefore plays an important part in the electrolyte's conductive ability. This is surprising as it is known that in swollen polymer electrolytes the liquid solvents ensure both the ionic dissociation and the ionic mobility, while the main function of the polymer matrix is to provide suitable mechanical properties, allowing the electrolyte to be shaped into thin membranes. In addition, the repeat unit of PAN is very close to that of PMAN, even if the donicity of the tertiary nitriles (in PMAN) is probably increased as compared to the secondary nitriles (in PAN) by the +I inductive effect induced by the methyl substituent. We assume that on the one hand, the spacing resulting from the cross-linking decreases the nitrile/nitrile interactions in the case of PMAN networks. Due to the electron withdrawing effect of nitrile, the C-H bond (of PAN) is slightly polarized with a partial positive charge on the hydrogen. Hydrogen bonds between C-H and nitrile should still increase the chain-chain interaction in PAN electrolyte and decrease the ionic mobility.

The conductivity comparison between the liquid electrolyte alone and the networks swollen by the same electrolyte shows that the ratio between their conductivities does not exceed a factor 2, this

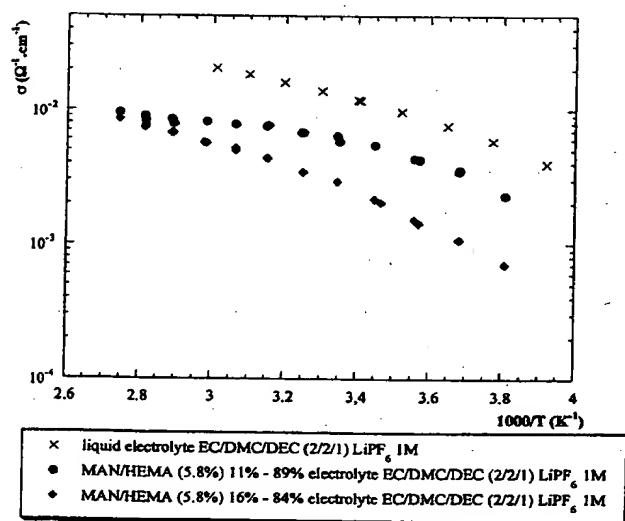


Figure 3. Conductivity plots vs. T^{-1} : comparison between liquid electrolyte and swollen MAN/HEMA networks.

Table V. Comparison of T_g values of the liquid electrolyte, the dry cross-linked copolymer, and the swollen network electrolyte.

	Copolymer B1	EC/DMC/DEC (2/2/1) LiPF ₆ 1 mol L ⁻¹	B1 + EC/DMC/DEC (2/2/1) LiPF ₆ 1 mol L ⁻¹
T_g (°C)	58.5	-99.7	-75.1

ratio decreasing when the temperature increases. This low difference is a clear advantage for PMAN networks with respect not only to PAN but also to microporous separators.^{28,29}

Figure 2 compares the conductivities of B1 and B2 swollen by the previous electrolyte, but at two swelling ratios, *i.e.*, 83 and 89%. The conductivities of both B1- and B2-based membranes decrease when decreasing the amount of solvent. However, even the less conductive electrolyte reaches 2 mS/cm at 20°C. A lower swelling ratio improves the mechanical strength of the membrane and therefore allows film thickness to be decreased, but it also allows the electrolyte cost to be decreased. Lastly, an optimization of the network microstructure might allow the conductivity drop to be decreased when the swelling ratio is lowered.

A free volume behavior is generally observed for concentrated liquid electrolyte, molten salt,³⁰ and was also reported in swollen polymer electrolytes.³¹

The conductivity evolution for B1, B2, and B3 swollen by 89% solvent and for the liquid electrolyte seems to follow a Vogel-Tamman-Fulcher (VTF) type law. T_0 , the ideal glass transition temperature, and pseudoactivation energy, E_a , are gathered in Table IV

$$\sigma(T) = \frac{A}{\sqrt{T}} \exp\left(\frac{-E_a}{k(T - T_0)}\right)$$

The comparison between T_0 of liquid electrolyte and those of the networks shows that due to the incorporation of rigid polymer chains, T_0 increases noticeably. T_0 values of B1, B2, and B3 are close to T_g values reported for swollen polymer electrolytes.³² Low values of E_a are obtained, consistent with conductivities slightly dependent on the temperature in liquid electrolytes.

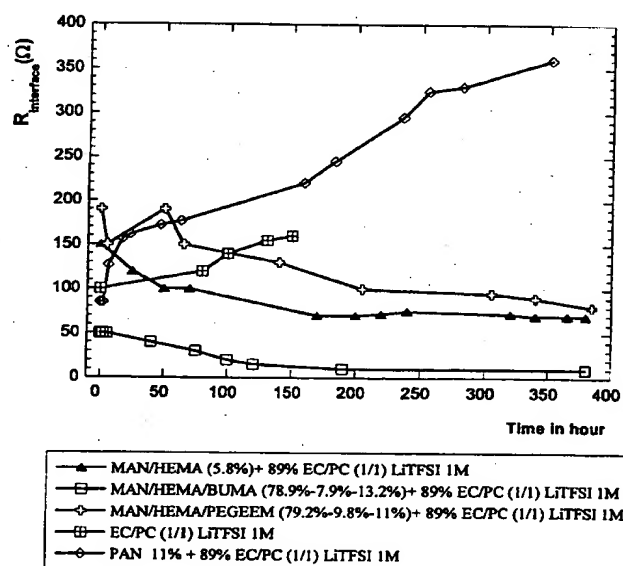


Figure 4. Interface resistance evolution with time for liquid electrolyte and swollen electrolyte networks.

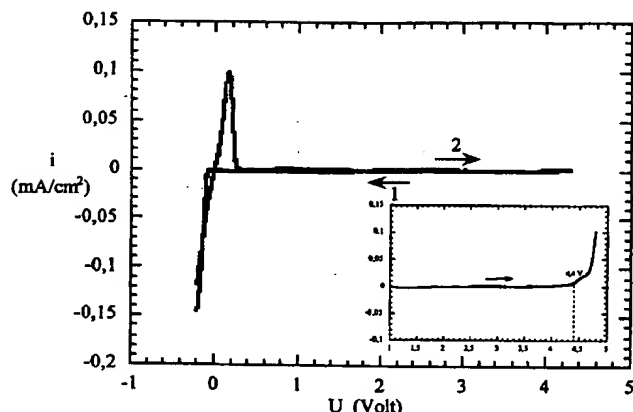


Figure 5. Cyclic voltammetry of B2 network swollen, at 89%, by a molar solution of LiTFSI in EC/PC (1/1 in volume). Temperature 30°C, sweep rate 7 mV min⁻¹, working electrode stainless steel.

Ionic conductivity of networks swollen by LiPF₆ electrolyte.—We selected membrane B1, which presents the best compromise between mechanical strength and conductivities, and used it to prepare networks swollen by the following electrolyte EC/DMC/DEC (2/2/1), LiPF₆ 1 mol L⁻¹. Besides the use of LiPF₆ instead of LiTFSI, propylene carbonate has been replaced by a mixture of acyclic carbonates DMC and DEC. The latter have a poor dielectric constant, a donor number close to the cyclic carbonates, but are known to significantly decrease the electrolyte viscosity, in particular, at low temperature.

Two swelling ratios were compared. The first one with 11% B1 and 89% of liquid electrolyte (10.4% salt and 78.6% solvent mixture), the second one with 16% B1, 84% electrolyte (9.8% salt and 74.2% solvent mixture). The second swelling ratio, i.e., 84%, corresponds to the swelling equilibrium at ambient temperature. This liquid electrolyte based on LiPF₆ is more conductive than the previous one based on LiTFSI in the entire temperature range (Fig. 3), the conductivity reaching 10 mS cm⁻¹ from 20°C. Figure 3 shows that the increase in swelling ratio leads to a significant increase in conductivity. The highest swelling ratio leads to a decrease in the network conductivity by a factor of 1.6 with respect to the pure liquid electrolyte. However, even the lowest swelling ratio provides a conductivity of 3 mS cm⁻¹ at 20°C. Still again the use of swollen B1 network does not result in a dramatic increase in the electrolyte resistivity. This might be due to the slight T_g increase induced by the use of PMAN networks. Indeed 1 M solution of LiPF₆ in EC/DMC/DEC (2/2/1) exhibits a T_g of -99.7°C while that of the network swollen by 89% of this liquid electrolyte remains very low, i.e., -75.1°C (Table V).

Electrochemical stability investigations.—Impedance analyses of symmetrical cells Li/electrolyte/Li were performed to compare the interfacial resistances of the different swollen network electrolytes. As the stability of LiPF₆ vs. metallic lithium is questionable, this study was performed on LiTFSI-based electrolytes. The cell was maintained at 30°C for more than 2 weeks. The interfacial resistances remain constant and even decrease for the three kinds of swollen network electrolytes (Fig. 4). They are slightly lower than that of the pure liquid electrolyte.

The same experiment on PAN swollen by the same electrolyte shows a continuous increase in interfacial resistance, in accordance with other results.¹⁶ These first investigations reinforce our choice to replace PAN by PMAN network which allows the electrolyte/lithium interface stability to be improved.

The cyclic voltammetry performed at 30°C, over a potential range from -0.1 to 4.8 V vs. Li/Li⁺ with stainless steel as the

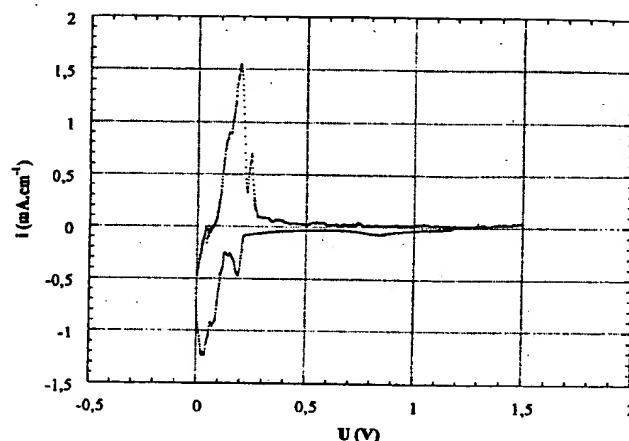


Figure 6. Cyclic voltammetry performed on B1 network swollen by LiPF₆ ternary liquid electrolyte on graphite electrode. Sweep rate 40 mV/h, temperature 30°C.

working electrode, on sample B2 swollen by LiTFSI electrolyte is reported in Fig. 5. A fairly good stability during the reduction reaction is observed, although the lithium plating-stripping only affords a yield close to 75% on average over the first eight cycles. The oxidation wall started near 4.4 V vs. Li/Li⁺. This oxidation must be attributed to the copolymer oxidation as the oxidation of the anion TFSI⁻ is observed near 5.7 V vs. Li/Li⁺.^{33,34} The oxidation wall potential is close to that reported with PAN/EC/PC/LiTFSI electrolyte.¹⁶

Lithium insertion was investigated using the B1 network swollen by LiPF₆ ternary liquid electrolyte. The reduction scan, Fig. 6, shows three peaks at respectively 0.1, 0.2, and 0.35 V vs. Li/Li⁺. Each peak is related to a stage of transition of lithium insertion into graphite electrode and in accordance with the four main stages of lithium insertion into graphite.³⁵ The reversible capacity is 3.18 mAh cm⁻² (326 mAh g⁻¹), while at the first cycle, the irreversible one is 0.15 mAh cm⁻² (15.4 mAh g⁻¹), representing 4.5% of the total capacity. The cyclic voltammetry shows the swollen network electrolyte stability vs. this negative electrode.

Conclusion

PMAN networks are promising materials for lithium-ion polymer batteries, as their swelling by usual liquid electrolytes allows very high conductivities to be reached. In addition, the curing prevents the polymer from being dissolved and the resulting electrolytes are stable at least up to 90°C. The electrochemical investigations performed with these electrolytes support our initial assumption that a substitution of hydrogen by a methyl group in polynitriles should improve the electrolyte stability in reduction with regard to PAN electrolytes. They are in agreement with our comparative investigations on molecules reproducing the repeat monomer units of PMAN and PAN. The first data obtained with graphite negative electrode are very encouraging. Further studies will deal with the design of a lithium-ion polymer battery adapted to PMAN networks and allow their complete evaluation with regard to cyclability, self-discharge, etc.

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